

S 4 5 - 7 5 6 6

(52) Japanese Classification

99 D 13

5

97(5) D 112

12 A 25

Japan Patent Office

(11) Patent Publication (Kokoku) No. S45-7566

(10) Official Gazette for Patent Publications

10

(44) Publication Date: March 16, 1970

Number of Inventions: 1

(Total of 3 pages [in the original])

(54) Method for Manufacturing Alkali Metal Vapor
Generator

15

(21) Application No. S41-72855

(22) Filing Date: November 7, 1966

(72) Inventor: Yoshikatsu Yasaka

c/o Tokyo Shibaura Denki Kabushiki Kaisha,
Horikawa Plant, 72 Horikawacho, Kawasaki-shi

20

(72) Inventor: Asomi Matsumura

c/o Tokyo Shibaura Denki Kabushiki Kaisha,
Horikawa Plant, 72 Horikawacho, Kawasaki-shi

(72) Inventor: Naofumi Ebihara

c/o Tokyo Shibaura Denki Kabushiki Kaisha,
Horikawa Plant, 72 Horikawacho, Kawasaki-shi

25

(72) Inventor: Haruo Takashio

c/o Tokyo Shibaura Denki Kabushiki Kaisha,
Horikawa Plant, 72 Horikawacho, Kawasaki-shi.

(72) Inventor: Tomiya Sonoda

c/o Tokyo Shibaura Denki Kabushiki Kaisha,
Horikawa Plant, 72 Horikawacho, Kawasaki-shi

(71) Applicant: Tokyo Shibaura Denki Kabushiki Kaisha
Horikawa Plant, 72 Horikawacho, Kawasaki-shi

Representative: Toshio Tsuchimitsu

Agent: Kazuo Inoue, Patent Attorney

Detailed Description of the Invention

The present invention relates to an improved method for manufacturing a cesium vapor generator used in the formation of the photoelectron emission surface of a photoelectric tube of an image orthicon or the like.

Conventional alkali metal vapor generators used to form the photoelectron emission surface of an image orthicon were produced as follows. A tubular vessel made of a material such as nickel, formed with a spiral cross sectional shape and provided with the desired opening in the lengthwise direction, was packed with a specific amount of a mixed powder comprising 1 weight part of at least one type of alkali metal chromate or dichromate and 2 weight parts of at least one type of reducing agent such as silicon, titanium, aluminum, or

zirconium, after which the vessel was sealed at both ends to produce an alkali metal vapor generator.

5 The above-mentioned mixed powder was obtained by combining the conventional raw materials, that is, the above-mentioned alkali metal salt and a reducing agent, in a specific ratio and then pulverizing the mixture. A alkali metal vapor generator produced in this manner was installed at the desired location in the tube vessel of an image orthicon, for instance, an alkali
10 metal vapor was generated by chemical reaction of the mixed powder brought about by electrically heating the tubular vessel, for example, and the alkali metal was vapor-deposited onto a metal thin-film formed on the inner surface of a face plate. Because the alkali
15 metal salt powder and reducing agent powder that form the mixed powder each had a wide range of particle sizes, the powders did not come into contact very evenly, which resulted in fluctuations in the chemical reaction velocity. Consequently, the amount of alkali
20 metal vapor generated per unit of time also fluctuated, which adversely affected the uniformity of the photoelectron emission surface. Fluctuation of the reaction velocity also made it difficult to accurately control the amount of metal vapor being generated,
25 diminished the characteristics of the photoelectron emission surface and a secondary electron multiplier,

and also lowered image quality and shortened the service life of the tube.

The present invention provides a method for manufacturing an alkali metal vapor generator in which the above drawbacks encountered in the past are ameliorated.

The inventors discovered that with an alkali metal vapor generator comprising a mixed powder of chromate powder of an alkali metal such as sodium, potassium, cesium, or rubidium, and a reducing agent powder composed of at least one member of the group consisting of silicon, titanium, aluminum, and zirconium, there are optimal ranges for the particle size of chromate powder and the reducing powder in order to generate an alkali metal vapor stably. Specifically, with a mixed powder in which the particle size ranges of the above two powders are each limited to specific values, contact between the chromate powder and the reducing agent powder is better, and therefore the reaction velocity of the two powders is more consistent and the alkali metal vapor is generated more stably.

The goal of limiting the particle size ranges of the alkali metal chromate powder and reducing agent powder to specific values is not achieved with a conventional method in which the raw materials are mixed in a specific ratio and then pulverized.

To use the pulverization of silicon and cesium chromate as an example, the hardness of silicon is far greater than that of cesium chromate, which results in just the cesium chromate being pulverized and the majority of the coarse particles of silicon not being pulverized. Furthermore, if the mixing and pulverization steps are carried out at substantially the same time, the state of contact between the particles of the two powders is affected by the atmosphere in which the steps are performed, and particularly by moisture.

With the method of the present invention, the raw materials, namely, the alkali metal chromate and the reducing agent, are each pulverized separately under specific conditions to obtain a powder having the desired particle size distribution, and only then are these powders mixed in a specific ratio. In the step of mixing the powders, it is preferable for the powders not to be pulverized to below the desired particle size range, so a mixture procedure that involves as little pulverizing action as possible should be employed.

A generator that affords even more stable reaction can be obtained by removing any coarse particles that may be contained in each of the constituent powders that have undergone the above-mentioned pulverization step. For example, good results will be obtained by

removing any coarse particles of cesium chromate of 200 mesh (Taylor sieve; the same applies hereinafter) or larger, or of the silicon in the reducing agent of 150 mesh or larger. This is because coarse particles of cesium chromate react violently and unstably, while coarse particles of silicon have a smaller surface area, so even if the cesium chromate particles are small, good and uniform contact will not be obtained between the two powders, and the reaction velocity will be inconsistent. Also, if the silicon powder particles are large, contact cohesion will occur among the cesium chromate powder particles, which can lead to a sudden reaction just as when coarse particles of cesium chromate are contained.

Furthermore, a generator that affords an even more stable reaction can be obtained by removing the mixed powder from the mixer during the mixing step after the above-mentioned chromate and reducing agent have been separately pulverized, drying the mixed powder, passing it through a 150 to 200 mesh sieve, removing any particles that do not pass through the sieve, then resuming the mixing, and repeating this procedure a few times. This procedure results in improved dispersion of the alkali metal chromate powder and reducing agent powder and in even better uniformity of the mixture, so a stable reaction is achieved.

The present invention will now be described through examples.

Example 1

Cesium chromate raw material was heated and dried, after which 3.0 g thereof was collected and put into a stainless steel pot (internal volume of 150 mL) along with stainless steel balls. The mill was run at 118 rpm to pulverize the contents for 15 minutes and obtain a cesium chromate powder. Meanwhile, silicon raw material was washed with acid and then washed with water and dried, after which it was put into a stainless steel pot (internal volume of 150 mL) along with stainless steel balls. The mill was run at 118 rpm to pulverize the contents for 40 minutes and obtain a silicon powder.

The above two powders were combined and mixed for 60 minutes in a stainless steel V mixer, after which they were taken out of the mixer and dried to obtain a mixed powder of cesium chromate powder and silicon powder. A tubular vessel made of nickel, formed with a spiral cross sectional shape and provided with the desired opening in the lengthwise direction, was packed with a specific amount of this mixed powder, after which the vessel was sealed at both ends to form a cesium vapor generator.

This generator and a generator obtained by packing a vessel the same as that described above with a mixed powder produced by a conventional method were each electrically heated by a specific current in a vacuum vessel so as to generate cesium vapor, and the reproducibility of the generation states were compared.

The reproducibility (that is, the ratio of the number of conforming articles out of the total sample) was 40 to 50% with the generator produced by the conventional method, but was 80% with the generator of this example.

Example 2

A cesium chromate powder that had been pulverized under the same conditions as in Example 1 was passed through a 200 mesh sieve to remove the coarse particles. Also, a silicon powder that had been pulverized under the same conditions as in Example 1 was passed through a 150 mesh sieve to remove the coarse particles.

The two powders from which the coarse particles had been removed were combined and mixed for 60 minutes in a V mixer, after which the mixed powder was taken out and dried. A specific amount of this mixed powder was packed into the same vessel as in Example 1 to produce a cesium vapor generator. This generator and a generator produced by a conventional method were compared in the same manner as in Example 1, which

revealed that the reproducibility of the generator of this example was 82 to 84%, whereas that of the conventional generator was 40 to 50%, indicating that the results were even better than the 80% of Example 1.

5 Example 3

Raw material cesium chromate and silicon were pulverized under the same conditions as in Example 1, after which the cesium chromate powder thus obtained was passed through a 200 mesh sieve to remove the
10 coarse particles. The silicon powder was passed through a 150 mesh sieve to remove the coarse particles.

The two powders from which the coarse particles had been removed were combined and mixed for 30 minutes in a V mixer, after which the mixed powder was taken
15 out and heated and dried for 30 minutes at 100°C, and then the mixture was passed through a 60 mesh sieve. The mixed powder that passed through this sieve was put back into the V mixer and mixed for 30 minutes.

Upon completion of this mixing, a specific amount
20 of this mixed powder was packed into the same vessel as in Example 1 to produce a cesium vapor generator. The reproducibility of this generator and that of a conventional generator were compared in the same manner as in Example 1, which revealed that the
25 reproducibility of the generator of this example was 86 to 90%, indicating that the results were even better

than those obtained with the generators of Examples 1 and 2.

5 A mixed powder of cesium chromate and silicon was produced in the examples given above, but the results are similar when producing a multi-alkali generator using one or more chromates or dichromates of alkali metals such as cesium, sodium, potassium, rubidium, and lithium, either in elemental or compound form.

10 Also, the same results are obtained when one or more members of the group consisting of titanium, aluminum, zirconium, and the like, either in elemental or alloy form, are selected and used either in elemental or compound form instead of silicon for the reducing agent.

15 The effect of the method of the present invention will be the same when the above-mentioned mixed powder is molded into pellets and an alkali metal vapor generator is formed.

20 With the method of the present invention, it is possible to obtain an alkali metal vapor generator with which an alkali metal vapor can be generated stably and with accurate control over the amount being generated, and therefore this method offers excellent practical benefits in the formation of the photoelectron emission surface of a photoelectric tube, such as a

25

photoelectron multiplier tube or ultraviolet
fluorescence multiplier tube, of an image orthicon.

Claims

1 A method for manufacturing an alkali metal
5 vapor generator, comprising the steps of:

obtaining a powder whose particle size is within a
specific range by pulverizing at least one type of
alkali metal chromate or dichromate;

10 obtaining a reducing agent powder whose particle
size is within a specific range by pulverizing at least
one member of the group consisting of silicon, titanium,
aluminum, and zirconium, either in elemental or alloy
form; and

15 combining and mixing specific amounts of the
alkali metal salt powder and the reducing agent powder.

Reference Literature

Japanese Patent Publication S35-3660

Translator's note:

Page 3, column 5, line 16, literally "outer" (*gai*) in the original, but this doesn't seem to make any sense. Ultraviolet (*shigai*) is a best guess as to the intended meaning.

5

⑤日本分類

99 D 13

97(5) D 112

12 A 25

日本國特許庁

特許公報

①特許出願公告

昭45-7566

④公告 昭和45年(1970)3月16日

発明の数 1

(全3頁)

1

②アルカリ金属蒸気発生器の製作方法

③特 願 昭41-72855

③出 願 昭41(1966)11月7日

③発 明 者 八坂頼勝
川崎市堀川町72東京芝浦電気株
式会社堀川町工場内

同 松村阿曾美

同所

同 海老原直文

同所

同 高塩治男

同所

同 園田富也

同所

⑦出 願 人 東京芝浦電気株式会社
川崎市堀川町72

代 表 者 土光敏夫

代 理 人 井理士 井上一男

発明の詳細な説明

本発明はイメージオルシコン等の光電管の光電子放射面の形成に使用するセシウム蒸気発生器の製造方法の改良に関する。

従来イメージオルシコンの光電子放射面の形成に使用されるアルカリ金属蒸気発生器はアルカリ金属のクロム酸塩若しくは重クロム酸塩の少なくとも1種の1重量部とシリコン、チタン、アルミニウムおよびジルコニウム等の還元剤の少なくとも1種2重量部との混合粉末を、断面渦巻状に形成し長手方向に所望の開口部を設けた例えばニッケル製の管状容器に所定量充填した後、容器の両端部を封止してアルカリ金属蒸気発生器を製作している。

前記混合粉末は従来原料の前記アルカリ金属塩と還元剤とを所定比率で合併後粉砕して混合粉末を得ている。このようにして製作されたアルカリ金属蒸気発生器を例えばイメージオルシコンの管

容器内の所望の位置に装填し、例えば管状容器に通電加熱して前記混合粉末の化学反応によつてアルカリ金属蒸気を発生せしめフェースプレート内表面に形成された金属薄膜上にアルカリ金属を蒸着する。しかるに前記混合粉末を形成しているアルカリ金属塩粉末および還元剤粉末はそれぞれ広範囲の粒度範囲を持つている故両粉末の接触状態は均一性を欠き化学反応速度の変動を生ずる。したがつて単位時間に発生するアルカリ金属蒸気の発生量も変動し光電子放射面の一様性を損なう。また反応速度の変動は金属蒸気発生量の正確な制御を困難にし光電子放射面および二次電子増倍部の特性を損ない、さらに撮像画質および管の寿命の低下をも招く欠点を有していた。

15 本発明は前記従来の欠点を改良したアルカリ金属蒸気発生器の製造方法を提供するものである。

本発明者等はナトリウム、カリウム、セシウム、ルビジウム等のアルカリ金属のクロム酸塩粉末と、シリコンチタン、アルミニウムおよびジルコニウム等の少なくとも1種からなる還元剤粉末と

20 の混合粉末からなるアルカリ金属蒸気発生器においてアルカリ金属蒸気を安定に発生するためには前記クロム酸塩粉末および還元剤粉末にそれぞれ最適の粒度範囲があることを見出した。すなわち前記両粉末の粒度範囲をそれぞれ所定の値に規制した混合粉末においてはクロム酸塩粉末と還元剤粉末との接触が良好となり、したがつて両者の反応速度が一定となりアルカリ金属蒸気の発生は安定する。

25 前記アルカリ金属のクロム酸塩粉末および還元剤粉末の粒度範囲をそれぞれ所望の値に規制するためには従来の如く各原料を所定の比率に合併した後粉砕する方法では目的を達し得ない。

と言うのはけい素とクロム酸セシウムの粉砕に例をとると両者の硬度は圧倒的にけい素が大であるのでクロム酸セシウムだけが粉砕される結果となつてけい素の粗大粒子の大部分が粉砕されない結果をもたらす。更に混合工程と粉砕工程を殆

2

と同時に付た場合両粉末粒子の接触状態が前記工程の実施される雰囲気特に水分に影響される。

本発明方法においてはアルカリ金属のクロム酸塩と還元剤との各原料をそれぞれ別個に所定の条件で粉砕し所望の粒度分布を有する粉末とした後これらの粉末を所定の比率に混合するものである。前記粉末の混合工程では粉末が粉砕され所望の粒度範囲から外れることは好ましくないから出来るだけ粉砕作用の少ない混合方式をとる。

さらに前記粉砕工程を経た各成分粉末中に若干混在している粗大粒子を除去することによつて一段と安定した反応を示す発生器を得ることが出来る。例えばクロム酸セシウムでは200メッシュ(テラー篩、以下同じ)以上、還元剤のシリコンでは150メッシュ以上の粗大粒子を除去すると好結果が得られる。これはクロム酸セシウムの粗大粒子は反応が激烈で不安定であり、またシリコンの粗大粒子は表面積が小さくなるため一方のクロム酸セシウムがたとえ小粒子であつても均一良好な両者の接触は得られず反応速度が不均一となる。またシリコン粉末粒子が大きい場合クロム酸セシウム粉末粒子同志の接触凝集を生じクロム酸セシウムの粗大粒子を含むのと同様に急激な反応の原因となる。

さらに前記アルカリ金属のクロム酸塩と還元剤とを別個に粉砕した後の混合工程中で混合粉末を混合機から取り出し乾燥して150~200メッシュの篩を通し前記篩を通過しない粒子を除去した後再び混合を続ける操作を数回繰返し行うことによつて一層安定した反応を示す発生器を得ることが出来る。前記操作によつてアルカリ金属のクロム酸塩粉末と還元剤粉末との分散が改善され混合物の均一性が一段と良好になるために安定した反応が得られるものである。

つぎに実施例について本発明を説明する。

例 1

原料のクロム酸セシウムを加熱乾燥した後、その3.0gをとり、内容積150mlのステンレス製ボットにステンレス製ボールとともに装入し毎分118回転で15分間粉砕してクロム酸セシウム粉末を得る。一方原料のシリコンを酸洗浄、水洗、乾燥の後、内容積150mlのボールミルにステンレス製ボールとともに装入し毎分118回転で40分間粉砕してシリコン粉末を得る。

前記両粉末を合併しステンレス製Vミキサーで

60分間混合した後ミキサーから取り出し乾燥してクロム酸セシウム粉末とシリコン粉末との混合粉末を得る。この混合粉末を断面渦巻状に形成し長手方向に所望の開口部を設けたニッケル製の管5状容器に所定量充填した後、容器の両端部を封止してセシウム蒸気発生器を形成する。

この発生器と従来方法で作成した混合粉末を前記と同様の容器に充填して得た発生器とを真空容器内で所定電流を通電加熱しセシウム蒸気を発生10せしめその発生状態の再現性を比較した。

再現率即ち全試料中良品数の比率は従来方法によるもの40~50%であつたのに対し本実施例のものは80%を示した。

例 2

例1と同様操作条件で粉砕したクロム酸セシウム粉末を200メッシュの篩を通して粗大粒子を除去する。また例1と同様操作条件で粉砕したシリコン粉末を150メッシュの篩を通して粗大粒子を除去する。

前記粗大粒子を除去した両粉末を合併しVミキサーで60分間混合した後混合粉末を取り出して乾燥する。この混合粉末を前記例1と同様の容器に所定量充填してセシウム蒸気発生器を作成する。この発生器と従来方法による発生器とを例1と同様に比較したところ本実施例の再現性は82~84%であつて従来品の40~50%はもとより例1の80%よりも良好な結果を示した。

例 3

原料のクロム酸セシウムおよびシリコンを例1の粉砕条件で粉砕した後、得られたクロム酸セシウム粉末を200メッシュの篩を通して粗大粒子を除去する。またシリコン粉末を150メッシュの篩を通して粗大粒子を除去する。

前記粗大粒子を除去した両粉末を合併しVミキサーで30分間混合した後混合粉末を取出し100℃で30分間加熱乾燥してから混合物を60meshの篩を通す。前記篩を通した混合粉末を再びVミキサーに装入し30分間混合する。

混合を終った混合粉末を前記例1と同様に容器に所定量充填してセシウム蒸気発生器を作成する。例1と同様に本実施例品と従来品のセシウム蒸気の再現性を比較したところ本実施例品は再現率86~90%であつて従来品および例1および例2の発生器よりも良好な結果を示した。

以上クロム酸セシウムとシリコンの混合粉末を

製作する例について説明したが、セシウム、ナトリウム、カリウム、ルビジウムおよびリチウム等のアルカリ金属のクロム酸塩もしくは重クロム酸塩を単独で用い、または複合で用いてマルチアルカリ発生器を得る場合にも適用し得る。

また還元剤にシリコンの他タタン、アルミニウムおよびジルコニウム等の単体又は合金の中から選択し単独または複合で使用する場合にも同様の効果を有する。

さらに前記混合粉末をペレット状に成形してアルカリ金属蒸気発生器を形成する場合にも本発明方法の効果は変りない。

本発明の方法によればアルカリ金属蒸気発生が安定して発生量の制御が正確に行えるアルカリ金属蒸気発生器を得ることが出来るからイメージオルシコンの外装光増倍管、光電子増倍管等の光電

管の光電子放射面の形成に優れた実用上の効果を有するものである。

特許請求の範囲

- 1 アルカリ金属のクロム酸塩若しくは重クロム
- 5 酸塩の少なくとも1種を粉砕して所定の粒度範囲の粉末を得る工程と、シリコン、タタン、アルミニウムおよびジルコニウム単体又は合金の少なくとも1種を粉砕して所定の粒度範囲の還元剤粉末を得る工程と、前記アルカリ金属塩粉末と還元剤
- 10 粉末とを所定量合併し混合する工程とを具備することを特徴とするアルカリ金属蒸気発生器の製作方法。

15 参考文献

特 公 昭35-3660